

5

ALIPHATIC POLYCARBONATE HOMO- AND CO-POLYMERS  
PRODUCED BY DMC CATALYSIS  
AND THE PROCESS FOR THEIR PRODUCTION

BACKGROUND OF THE INVENTION

The invention relates to aliphatic polycarbonate homo- and co-  
10 polymers which are obtained by ring-opening homo- or co-polymerization  
of cyclic carbonates by DMC catalysis.

Double metal cyanide (DMC) catalysts useful for the ring-opening  
polymerization of oxygen-containing, cyclic monomers have been known  
15 for a long time. DMC catalysts are of particular commercial interest for the  
production of polyether polyols by polyaddition of epoxides to starter  
compounds exhibiting active hydrogen atoms (See, e.g., U.S. Patents  
3,404,109; 3,829,505; 3,941,849 and 5,158,922.) because the use of a  
DMC catalyst reduces the proportion of monofunctional polyethers with  
20 terminal double bonds (so-called "mono-ols") compared to polyether  
polyols produced using conventional alkaline catalysts. Moreover,  
improved, highly active DMC catalysts, which are described, e.g., in U.S.  
Patent 5,470,813; EP-A 700 949; EP-A 743 093; EP-A 761 708; WO  
97/40086; WO 98/16310 and WO 00/47649, possess extraordinarily high  
25 activity and permit polyether polyol production at very low catalyst  
concentrations (25 ppm or less). Consequently, it is no longer necessary  
to separate the catalyst from the finished product. In addition, DMC  
catalysts also make possible the homo- and co-polymerization of other  
oxygen-containing, cyclic monomers, such as oxetanes, (U.S. Patents  
30 3,278,457 and 3,404,109), cyclic anhydrides (U.S. Patents 5,145,883 and  
3,538,043) and lactones (U.S. Patent 5,032,671).

Aliphatic polycarbonate homo- and co-polymers are suitable as  
additives for thermoplastic systems. Moreover, aliphatic, OH-functional

"Express Mail" mailing label number EV 23688355 US  
Date of Deposit September 2, 2003

I hereby certify that this paper or fee is being deposited with the United States Postal Service  
"Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated  
above and is addressed to the Commissioner of Patents and Trademarks,  
Alexandria, VA 22313-1450.

Karen Lockhart

(Name of person mailing paper or fee)

Signature of person mailing paper or fee

polycarbonates are widely used as a hydroxyl component for building up polyurethanes and polyurethane-urea elastomers. Common methods for the production of aliphatic polycarbonates are transesterification of a diol with a dialkyl carbonate from a short-chain alcohol, with a dioxolanone or with a diphenyl carbonate. These reactions are accelerated by catalysts, particularly alkali, tin and titanium compounds (See, e.g., Kunststoffsandbuch, vol. 3/1 Polycarbonate, Hanser Verlag, Munich, 1992, p. 118 f.).

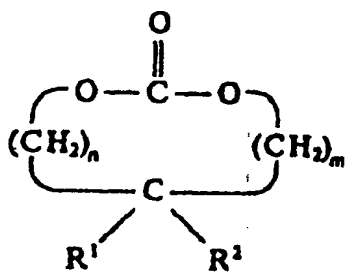
### SUMMARY OF THE INVENTION

It has now been found that aliphatic polycarbonate homo- and co-polymers can be obtained by ring-opening homo- or co-polymerization of a cyclic carbonate by DMC catalysis.

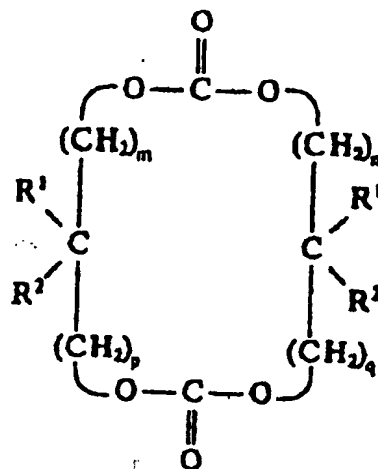
### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to aliphatic polycarbonate homo- and co-polymers, which are obtained entirely or partly by ring-opening homo- or co-polymerization of cyclic carbonates by DMC catalysis.

Suitable cyclic carbonates useful in the practice of the present invention may be represented by the general formula (I.) or (II.)



(I)



(II)

in which

m, n, p and q, independently of one another, each represents 0, 1, 2, 3, 4, 5 or 6 and

- 5     $R^1$  and  $R^2$  represent H, a  $C_{1-6}$  alkyl, a  $C_{3-6}$  alkenyl, or a  $C_{1-6}$  alk(en)oxy-  
 $C_{1-6}$  alkyl group, particularly H,  $CH_3$  and  $C_2H_5$ .

Preferred cyclic carbonates represented by formula (I) or (II) include: trimethylene glycol carbonate, neopentyl glycol carbonate, 1,4-  
10    butanediol carbonate and dimeric carbonates of pentanediol or of hexanediol. Particularly preferred are 6-membered ring carbonates, particularly neopentyl glycol carbonate.

Suitable DMC catalysts are known and are described in detail in the  
15    disclosures discussed in the Background of the Invention. Improved, highly active DMC catalysts, such as those described in U.S. Patent 5,470,813; EP-A 700 949; EP-A 743 093; EP-A 761 708; WO 97/40086; WO 98/16310 and WO 00/47649, are preferably used. The highly active DMC catalysts described in EP-A 700 949, which, in addition to a double metal  
20    cyanide compound (e.g. zinc hexacyano-cobaltate(III)) and an organic complex ligand (e.g. tert.-butanol), also contain a polyether with a number-average molecular weight of more than 500 g/mole, are typical examples of suitable catalysts.

25    The DMC-catalyzed, ring-opening homo- or co-polymerization of the cyclic carbonate generally takes place at temperatures of from 20 to 200°C, preferably in the range of from 40 to 180°C, most preferably at temperatures of from 80 to 160°C. The reaction can be conducted under a total pressure of from 0.001 to 20 bar. The polymerization can be  
30    performed in substance or in an inert, organic solvent, such as toluene or

tetrahydrofuran (THF). If used, the quantity of solvent is generally from 10 to 30 wt.%, based on the total amount of polymer to be produced.

The catalyst concentration is generally in the range of from  
5 0.0005 wt.% to 1 wt.%, preferably in the range of from 0.001 wt.% to 0.1 wt.%, most preferably in the range of from 0.001 to 0.05 wt.%, based on the total amount of polymer to be produced.

The polymerization can be performed continuously or non-  
10 continuously, e.g. in a batch or semi-batch process.

The DMC-catalyzed, ring-opening homo- or co-polymerization of the cyclic carbonate is optionally performed in the presence of one or more starter compounds exhibiting active hydrogen atoms. In this way, OH-  
15 functionalized aliphatic polycarbonate homo- and co-polymers that are suitable as polyol components for building up polyurethane systems can be produced.

Compounds with molecular weights of from 18 to 10,000 g/mole  
20 and having from 1 to 8 hydroxyl groups are preferably used as starter compounds exhibiting active hydrogen atoms. Examples of such compounds include: water, ethanol, butanol, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butanediol, hexamethylene glycol, bisphenol A, trimethylolpropane, glycerol,  
25 pentaerythritol, sorbitol, cane sugar, degraded starch, polyether polyols and polyester polyols.

The DMC-catalyzed, ring-opening polymerization of the cyclic carbonate can be performed as a homo-polymerization, optionally in the  
30 presence of one or more starter compounds exhibiting active hydrogen atoms.

The DMC-catalyzed, ring-opening polymerization of the cyclic carbonates can also be performed as a co-polymerization, again optionally in the presence of one or more starter compounds exhibiting active  
5 hydrogen atoms. Both random co-polymerization and block co-polymerization are possible.

In random co-polymerization, the DMC-catalyzed, ring-opening polymerization of the cyclic carbonate is performed in the presence of one  
10 or more other monomers suitable for polymerization with a DMC catalyst. Particularly suitable for random co-polymerization with cyclic carbonates are: epoxides, particularly ethylene oxide, propylene oxide and butylene oxide and mixtures thereof; oxetanes; cyclic anhydrides, such as phthalic anhydride; cyclic esters, such as caprolactone; and lactides.

15

In the production of polycarbonate block co-polymers in accordance with the present invention, the aliphatic polycarbonate block is obtained by means of DMC-catalyzed, ring-opening polymerization of a cyclic carbonate. Preferred block co-polymers include: poly(ester-block-  
20 carbonate) co-polymers and poly(ether-block-carbonate) co-polymers, in which the ester or ether block can be obtained by any of the known processes or catalysts.

In a preferred embodiment of the process of the present invention,  
25 a polyether polyol is first produced by any of the known methods, e.g., by DMC-catalyzed polyaddition of an epoxide, (particularly propylene oxide and/or a propylene oxide/ethylene oxide mixture), to the starter compound exhibiting active hydrogen atoms (mentioned above). The polyether polyol containing the active DMC catalyst is then reacted with a cyclic carbonate  
30 in the manner according to the present invention, with ring-opening. In this reaction with the carbonate, secondary hydroxyl groups of the polyether

polyol can be converted completely or partially into primary hydroxyl groups, which are more reactive with isocyanate groups. These poly(ether-carbonate) polyols are therefore of great interest for use in the production of polyurethanes.

5

Having thus described the invention, the following Examples are given as being illustrative thereof.

EXAMPLESExample 1

In a heatable, flat-ground jar equipped with a stirrer and reflux  
5 condenser, 20 g of a polypropylene glycol starter compound (number-  
average molecular weight = 1,000 g/mole) and 4 mg of DMC catalyst  
(containing zinc hexacyanocobaltate, tert.-butanol and polypropylene  
glycol with a number-average molecular weight of 1000 g/mole; described  
in EP-A 700 949) were placed under argon and heated to 105°C. 20 g of  
10 propylene oxide were then metered in continuously at 105°C under  
normal pressure within 3 hours. When all of the propylene oxide had been  
added, 5.2 g of neopentyl glycol carbonate were added and stirring was  
then continued for 1 hour at 150°C under normal pressure. Volatile  
components were then distilled off for 1 h at 150°C/1 mbar. The mixture  
15 was then cooled to ambient temperature.

A slightly yellowish, clear product was obtained. <sup>1</sup>H- and <sup>13</sup>C-NMR  
analysis showed that 28% of the secondary hydroxyl groups of the  
polypropylene glycol had reacted with neopentyl glycol carbonate, with  
20 ring opening, forming a primary hydroxyl group.

Example 2

In a heatable, flat-ground jar equipped with a stirrer and reflux  
condenser, 20 g of a polypropylene glycol starter compound (number-  
25 average molecular weight = 1,000 g/mole) and 2 mg of the DMC catalyst  
used in Example 1 were placed under argon and heated to 105°C. 20 g of  
propylene oxide were then metered in continuously at 105°C under normal  
pressure within 3 hours. When all of the propylene oxide had been added,  
5.2 g of neopentyl glycol carbonate were added and stirring was then  
30 continued for 5 hours at 150°C under normal pressure. Volatile

components were then distilled off for 1 h at 150°C/1 mbar and the reaction mixture was then cooled to ambient temperature.

5 A yellowish, clear product was obtained. <sup>1</sup>H- and <sup>13</sup>C-NMR analysis showed that 47% of the secondary hydroxyl groups of the polypropylene glycol had reacted with neopentyl glycol carbonate, with ring opening, forming a primary hydroxyl group.

### Example 3

10 In a heatable, flat-ground jar equipped with a stirrer and reflux condenser, 20 g of a polypropylene glycol starter compound (number-average molecular weight = 1,000 g/mole) and 2 mg of the DMC catalyst used in Example 1 were placed under argon and heated to 105°C. 20 g of propylene oxide were then metered in continuously at 105°C under normal  
15 pressure over 3 hours. When all the propylene oxide had been added, 15.6 g of neopentyl glycol carbonate were added and stirring was then continued for 1 hour at 150°C under normal pressure. Volatile components were then distilled off for 1 h at 150°C/1 mbar and the reaction mixture was then cooled to ambient temperature.

20

A yellowish and (because of unreacted neopentyl glycol carbonate) cloudy product was obtained. <sup>1</sup>H- and <sup>13</sup>C-NMR analysis showed that 70% of the secondary hydroxyl groups of the polypropylene glycol had reacted with neopentyl glycol carbonate, with ring opening, forming a primary  
25 hydroxyl group.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in  
30 the art without departing from the spirit and scope of the invention except as it may be limited by the claims.